

Extension of the Schiff theorem to ions and molecules

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According to the Schiff theorem the nuclear electric dipole moment (EDM) is screened in neutral atoms. In ions this screening is incomplete. We extend a derivation of the Schiff theorem to ions and molecules. The finite nuclear size effects are considered including $Z^2\alpha^2$ corrections to the nuclear Schiff moment which are significant in all atoms and molecules of experimental interest. We show that in majority of ionized atoms the nuclear EDM contribution to the atomic EDM dominates while in molecules the contribution of the Schiff moment dominates. We also consider the screening of electron EDM in ions.

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I. INTRODUCTION

Permanent electric dipole moment (EDM) of elementary particle or atom violates both P and T invariance. The Kobayashi-Maskawa mechanism leads to extremely small values of the EDMs of the particles. It is also too weak to explain the matter-antimatter asymmetry of the Universe. On the other hand, most of the popular extensions predict much larger EDMs which are within experimental reach. Therefore, measurements of EDM provide an excellent method to search for physics beyond the Standard Model. The measurements of EDM in atomic and molecular experiments are presented in Refs. [1–19].

The EDM of an atom is mostly due to either electron EDM and T, P -odd electron-nucleon interactions in paramagnetic systems (with non-zero electron angular momentum J) or due to the T, P -odd nuclear forces in diamagnetic systems ($J = 0$; nuclear-spin-dependent e-N interaction contributes here too). The existence of T, P -odd nuclear forces leads to the T, P -odd nuclear moments in the expansion of the nuclear potential in powers of distance R from the center of the nucleus. The lowest-order term in the expansion, the nuclear EDM, is unobservable in neutral atoms due to the total screening of the external electric field by atomic electrons [20]. It might be possible however to observe the nuclear EDM in ions, where it is screened incompletely (see e.g. [21–23]). The first non-vanishing terms which survive the screening in neutral systems are the Schiff moment which was defined in Ref. [24] (see also Refs. [25, 26] where the contribution of the proton EDM was considered) and the electric octupole moment (the latter vanishes in nuclei of experimental interest which have spin $1/2$). More accurate treatment of the finite nuclear size in Ref. [27] has shown that the atomic EDM is actually produced by the nuclear Local dipole moment which differs from the Schiff moment by a correction $\sim Z^2\alpha^2$ where Z is the nuclear charge and α

is the fine structure constant. Since all experiments deal with heavy atoms this correction is significant.

In the non-relativistic classical limit the screening formulas can be obtained in a very simple way. The second Newton law for the ion and its nucleus in the electric field reads

$$(M_N + N_e m_e) a_i = (Z - N_e) e E_0 \quad (1)$$

$$M_N a_N = Z e E_N \quad (2)$$

$$m_e a_e = e E_e, \quad (3)$$

where m_e and M_N are the electron and nuclear masses; a_i , a_N and a_e are the ion, nucleus and electron average accelerations respectively, E_0 is the external electric field, E_N is the average electric field at the nucleus, E_e is the average electric field at one of the ion electrons, e is the proton charge, N_e is the number of electrons in the ion. Since system of particles moves altogether, the averaged accelerations must be equal ($a_i = a_N = a_e$), therefore

$$E_N = \frac{Z - N_e}{Z} E_0 \frac{M_N}{M_N + N_e m_e} \approx (1 - N_e/Z) E_0 \quad (4)$$

$$E_e \approx (Z - N_e) \frac{m_e}{M_N} E_0. \quad (5)$$

As we can see, the average electric field for electrons is suppressed by the ratio of masses m_e/M_N that is very small for heavy atoms. It means that in the non-relativistic limit there is practically no effect related to the electron EDM in heavy atoms and ions, $-\mathbf{d}_e \cdot \mathbf{E}_e \approx 0$. The interaction of the nuclear EDM d with the external field, $-\mathbf{d} \cdot \mathbf{E}_N$, is suppressed by the factor $(Z - N_e)/Z$.

The same approach can be used to determine the electric field at the nucleus in a diatomic molecule:

$$(M_1 + M_2 + N_e m_e) a_i = (Z_1 + Z_2 - N_e) e E_0,$$

$$M_2 a_2 = Z_2 e E_{2N},$$

$$E_{2N} = \frac{Z_1 + Z_2 - N_e}{Z_2} \frac{M_2}{M_1 + M_2 + N_e m_e} E_0. \quad (6)$$

Screening is stronger for diatomic molecules because of the factor $M_2/(M_1 + M_2)$ that contains both nuclear

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masses. This indicates that the nuclear motion can not be ignored. We also see that in neutral atoms and molecules the field at the nucleus is zero, therefore the interaction of the nuclear EDM d with the screened electric field vanishes, $\mathbf{dE}_N=0$. Similarly,

$$E_e = (Z_1 + Z_2 - N_e) \frac{m_e}{M_1 + M_2 + N_e m_e} E_0. \quad (7)$$

The different screening laws of EDM in neutral atoms, ions and molecules raise a number of new questions. For example, is the screening term in the nuclear Schiff moment different in neutral atoms and ions? Can nuclear motion in molecules produce any additional effects which do not exist in a single atom? Are there any new effects of the electron density polarization in ions and molecules? Simple classical formulas presented above do not answer these questions. This motivates us to revisit the quantum Schiff theorem [20] and extend it to the cases of ions and molecules. We also derive a formula which more accurately takes into account the finite nuclear size and calculate corrections to the nuclear Schiff moment.

The present work is also motivated by new experiments. Effects of EDM in molecules are enhanced [25, 26, 28, 29]. This is why the molecular experiments are so popular now. Recently the EDM experiment has been started with molecular ions [18]. The EDM experiments with atomic ions in the storage rings have been considered too [19].

II. SCREENING OF EDM IN ATOMIC IONS

A. Nuclear EDM and Schiff moment

The charge distribution in a finite size nucleus can be written as $\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r})$, where $\int \rho_0 d^3r = 1$, $\delta\rho(\mathbf{r})$ is due to the P, T -odd interactions. The P, T -odd term in charge density leads to the nonzero nuclear dipole moment $\mathbf{d} = d\mathbf{I}/I = Ze \int d^3r \delta\rho \mathbf{r}$, where Ze is the nucleus charge, e is the proton charge. Let us define N_e as the number of electrons. If $N_e \neq Z$ a system is an ion. In a neutral atom ($N_e = Z$) our derivation is expected to give the same results as the Schiff theorem [20] including the effects of the finite nuclear size [24, 27].

The Hamiltonian of a single atom in an external electric field E_0 can be written in the following form:

$$\hat{H} = \hat{T} + \hat{V}_0 + \hat{V} + \hat{U} + \hat{W}, \quad (8)$$

where

$$\begin{aligned} \hat{T} &= \sum_i^{N_e} \frac{-\hbar^2}{2m_e} \frac{\partial^2}{\partial \mathbf{R}_i^2} - \frac{\hbar^2}{2M_N} \frac{\partial^2}{\partial \mathbf{q}_N^2}, \\ \hat{V}_0 &= \sum_{i>j}^{N_e} \frac{e^2}{|\mathbf{R}_i - \mathbf{R}_j|} - Ze^2 \sum_i^{N_e} \int d^3r \frac{\rho_0(r)}{|\mathbf{R}_i - \mathbf{q}_N - \mathbf{r}|}, \\ \hat{V} &= \sum_i^{N_e} e \mathbf{R}_i \mathbf{E}_0 - Ze \mathbf{q}_N \mathbf{E}_0, \\ \hat{U} &= -Ze^2 \sum_i^{N_e} \int d^3r \frac{\delta\rho(\mathbf{r})}{|\mathbf{R}_i - \mathbf{q}_N - \mathbf{r}|}, \\ \hat{W} &= -\mathbf{dE}_0. \end{aligned}$$

Here \mathbf{R}_i and \mathbf{q}_N are the radius-vectors of the electrons and nucleus correspondingly. The expression for \hat{U} can be expanded in powers of r/R_i since the nuclei size is small compared to the atomic scales. Let us keep the first two nonvanishing terms:

$$\begin{aligned} \hat{U} &= -\mathbf{d}e \sum_i^{N_e} \frac{\mathbf{R}_i - \mathbf{q}_N}{|\mathbf{R}_i - \mathbf{q}_N|^3} \\ &\quad - 4\pi \frac{Ze^2}{10} \int d^3r \delta\rho r^2 \mathbf{r} \sum_i^{N_e} \nabla_i \delta(\mathbf{R}_i - \mathbf{q}_N). \end{aligned}$$

In the above expansion the octupole term was omitted since it leads to the mixing of the states with high electron angular momentum and its contribution to the total atomic EDM is small [24].

Following Schiff let us define the operator

$$\hat{Q} = \frac{\mathbf{d}}{Ze} \frac{\partial}{\partial \mathbf{q}_N}. \quad (9)$$

It is easy to check that there is a relation between $[\hat{Q}, \hat{V}_0]$ and \hat{U}

$$\hat{U} = [\hat{Q}, \hat{V}_0] - 4\pi e \mathbf{S} \sum_i^{N_e} \nabla_i \delta(\mathbf{R}_i - \mathbf{q}_N) \quad (10)$$

$$\mathbf{S} = \frac{1}{10} \left\{ Ze \int d^3r \delta\rho r^2 \mathbf{r} - \frac{5}{3} \mathbf{d} \int d^3r \rho_0(r) r^2 \right\}, \quad (11)$$

where the expression for the Schiff moment \mathbf{S} has the same form as for a neutral atom [24]. Substituting expression for \hat{U} and $\hat{W} = [\hat{Q}, \hat{V}]$ into Eq. (8) we obtain

$$\hat{H} = \hat{H}_0 + [\hat{Q}, \hat{H}_0] - 4\pi e \mathbf{S} \sum_i^{N_e} \nabla_i \delta(\mathbf{R}_i - \mathbf{q}_N), \quad (12)$$

where $\hat{H}_0 = \hat{T} + \hat{V}_0 + \hat{V}$ is the Hamiltonian of the system in the external electric field without P, T -odd terms. The calculation gives the following result for the commutator

$$[\hat{Q}, \hat{H}_0] = -\frac{\mathbf{d}}{Ze} \frac{i}{\hbar} [\hat{H}_0, \mathbf{P}_N] = -\frac{\mathbf{d}}{Ze} M_N \hat{\mathbf{a}}_N, \quad (13)$$

where $\hat{\mathbf{a}}_N$ is the nuclear acceleration operator. To obtain the average value of the acceleration operator we can use the Ehrenfest theorem:

$$\langle \hat{\mathbf{a}}_N \rangle = \frac{\langle \mathbf{F} \rangle}{M_N} = \frac{(Z - N_e)e\mathbf{E}_0}{M_N}, \quad (14)$$

where F is the average force acting on the nucleus (see Eq. (1)). Substituting the above expression to Eq. (13) we obtain for the averaged commutator of \hat{Q} and \hat{H}_0 the following equation

$$\langle [\hat{Q}, \hat{H}_0] \rangle = - \left(1 - \frac{N_e}{Z} \right) d\mathbf{E}_0. \quad (15)$$

Substituting this result into Eq. (12) we obtain the effective Hamiltonian of the ion in the external electric field E_0 :

$$\hat{H} = \hat{H}_0 - \left(1 - \frac{N_e}{Z} \right) d\mathbf{E}_0 - 4\pi e\mathbf{S} \sum_i^{N_e} \nabla_i \delta(\mathbf{R}_i - \mathbf{q}_N). \quad (16)$$

Note that the derivation above is done in the adiabatic approximation assuming that we can average over electron motion when we calculate the nuclear motion, i.e. we assume $m_e \ll M_N$. If the number of electrons $N_e = Z$ the EDM term in the above expression vanishes, as the Schiff theorem predicts. In the ion case the nuclear EDM interacts with the average field $E_N = E_0(1 - N_e/Z)$ that acts on the ion's nucleus.

The last term in Eq. (16),

$$\hat{H}_w = -4\pi e\mathbf{S} \sum_i^{N_e} \nabla_i \delta(\mathbf{R}_i - \mathbf{q}_N), \quad (17)$$

induces the ion EDM directed along the nuclear spin (which is the direction of the nuclear Schiff moment \mathbf{S}), similar to the EDM of neutral atoms. This expression is not applicable for heavy atoms where the Dirac equation gives infinite results for the electron wave functions at the point-like nucleus. Accurate account of the finite nuclear size gives the following form for the corrected Schiff moment electrostatic potential (defined by $\hat{H}_w = -e\varphi_S(\mathbf{R})$):

$$\varphi_S(\mathbf{R}) = -\frac{3\mathbf{S}' \cdot \mathbf{R}}{B} \rho_0(R), \quad (18)$$

where $B = \int \rho_0(R) R^4 dR$ is the normalization constant. In the limit of the point-like nucleus the expression (18) agrees with Eq. (17). The corrected Schiff moment \mathbf{S}' is given by the equation (see Appendix)

$$\mathbf{S}' = \frac{Ze}{10} \frac{1}{1 - \frac{5}{14} Z^2 \alpha^2} \cdot \left\{ \left[\langle \mathbf{r} r^2 \rangle - \frac{5}{3} \langle \mathbf{r} \rangle \langle r^2 \rangle - \frac{2}{3} \langle r_i \rangle \langle q_{ij} \rangle \right] - \frac{5}{28} \frac{Z^2 \alpha^2}{R_N^2} \left[\langle \mathbf{r} r^4 \rangle - \frac{7}{3} \langle \mathbf{r} \rangle \langle r^4 \rangle - \frac{4}{3} \langle r_i \rangle \langle q_{ij} r^2 \rangle \right] \right\} \quad (19)$$

where q_{ij} is the quadrupole moment tensor. Here we omitted higher order terms which are proportional to a small factor $Z^4 \alpha^4 / 9$. Outside the nuclear radius R_N the nuclear density $\rho_0(R) = 0$ and the potential (18) vanishes in agreement with the Schiff theorem. Near the origin $\rho_0(R) = \text{const}$ and the potential (18) is a linear function of \mathbf{R} . Therefore, the gradient of the Schiff moment potential (18) gives a constant electric field inside the nucleus which is directed along the nuclear spin. This electric field polarizes the electron distribution and produces the atomic EDM. The calculations of the atomic EDM have been performed, for example, in Refs. [24, 30–32].

Below we make rough estimates to compare the nuclear EDM and the Schiff moment contributions to the atomic EDM. In the case of a spherical nucleus the nuclear EDM d , the nuclear Schiff moment and the atomic EDM D_A induced by the Schiff moment have been estimated in Ref. [24]:

$$d \sim 10^{-21} \eta e \cdot \text{cm}, \quad (20)$$

$$D_A \sim (Z/100)^2 \cdot 10^{-24} \eta e \cdot \text{cm}, \quad (21)$$

where η is the strength constant of the nuclear P, T -odd interaction (in units of the weak Fermi constant G). Assuming the single ionization we get for the nuclear EDM screening factor $1 - N_e/Z = 1/Z$. As a result, for the ionic EDM induced by the nuclear EDM we get the estimate $1/Z \cdot 10^{-21} \eta |e| \text{cm}$. Thus, for the spherical nuclei the nuclear EDM contribution exceeds the nuclear Schiff moment contribution by at least one order of magnitude. However, in heavy ions containing nuclei with the octupole deformation (e.g. $^{225}\text{Ra}^+$ and $^{223}\text{Rn}^+$) the Schiff moment contribution is enhanced by three orders of magnitude [33, 34] and is comparable to the nuclear EDM contribution (which is also slightly enhanced in these ions).

B. Electron EDM

For neutral atoms the electron EDM problem was investigated in [35] and further developed in [36]. The Hamiltonian of the nucleus and relativistic electrons in the external electric field E_0 can be presented as

$$\hat{H} = \hat{H}_0 + \hat{H}_w, \quad (22)$$

$$\begin{aligned} \hat{H}_0 = & -\hbar^2 \Delta_N / 2M_N - Ze\mathbf{q}_N \mathbf{E}_0 + \\ & \sum_i^{N_e} -i\hbar c \alpha_i \nabla_i + \beta_i m c^2 - \frac{Ze^2}{|\mathbf{R}_i - \mathbf{q}_N|} + \\ & e\mathbf{R}_i \mathbf{E}_0 + \sum_{j>i} \frac{e^2}{|\mathbf{R}_i - \mathbf{R}_j|} \end{aligned} \quad (23)$$

$$\hat{H}_w = -d_e \sum_i^{N_e} \beta_i \Sigma_i \mathbf{E}_t, \quad (24)$$

$$\Sigma = \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix}$$

where \mathbf{E}_t is the total electric field acting on the electron which includes the external field \mathbf{E}_0 , the nuclear field and the field of other electrons, α and β are the Dirac matrices. It is convenient to present H_w as the sum of two terms

$$\hat{H}_w = \hat{H}_{1d} + \hat{H}_{2d}, \quad (25)$$

$$\hat{H}_{1d} = -d_e \sum_i^{N_e} \Sigma_i \mathbf{E}_t, \quad (26)$$

$$\hat{H}_{2d} = -d_e \sum_i^{N_e} (\beta_i - 1) \Sigma_i \mathbf{E}_t. \quad (27)$$

As it was pointed in [35] the first term H_{1d} gives no contribution to atomic EDM in a neutral atom. In an ion the H_{1d} contribution is suppressed by a small factor m_e/M_N . It can be shown using the commutator relation

$$\hat{H}_{1d} = [\hat{Q}, \hat{H}_0], \quad (28)$$

$$\hat{Q} = -\frac{d_e}{e} \sum_i^{N_e} \Sigma_i \frac{\partial}{\partial \mathbf{R}_i}. \quad (29)$$

Note that the matrix elements of the operators in the the H_{1d} come from the atomic size area where valence electrons (which contribute to the atomic angular momentum and EDM) are non-relativistic. To estimate the average value of the commutator $[\hat{Q}, \hat{H}_0]$ the Ehrenfest theorem can be employed

$$\begin{aligned} \langle [\hat{Q}, \hat{H}_0] \rangle &= \frac{d_e}{e} \langle \sum_i \Sigma_i \frac{d\mathbf{p}_i}{dt} \rangle \\ \langle \sum_i \Sigma_i \frac{d\mathbf{p}_i}{dt} \rangle &\approx \langle \sum_i \Sigma_i \mathbf{F}_i \rangle = -e \langle \sum_i \Sigma_i \mathbf{E}_e \rangle \end{aligned} \quad (30)$$

Substituting expression (5) for \mathbf{E}_e into above equation we obtain for the average value of \hat{H}_{1d}

$$\langle \hat{H}_{1d} \rangle \approx -d_e \frac{m_e}{M_N} (Z - N_e) \langle \sum_i \Sigma_i \mathbf{E}_0 \rangle \quad (31)$$

We see that the averaged value $\langle \hat{H}_{1d} \rangle$ is suppressed by the small mass ratio m_e/M_N . It means, that in the limit of heavy nucleus \hat{H}_{1d} gives no contribution to EDM.

The second perturbation term \hat{H}_{2d} vanishes in the non-relativistic limit since the matrix $(\beta_i - 1)$ acts on the lower components of the Dirac 4-spinors only. The operator \hat{H}_{2d} induces atomic EDM given by the same expression as for neutral atoms, except for the sum in the matrix elements is taken over electron number $N_e < Z$:

$$\begin{aligned} \mathbf{D}_2 &= d_e \langle 0 | \sum (\beta_i - 1) \Sigma_i | 0 \rangle + \\ &2e d_e \sum_n \frac{\langle 0 | \sum (\beta_i - 1) \Sigma_i \mathbf{E}_t | n \rangle \langle n | \sum \mathbf{R}_i | 0 \rangle}{E_0 - E_n} \end{aligned} \quad (32)$$

In heavy atoms the major contribution to D_2 comes from the second term ($D_2 \sim 3R_{rel}Z^3\alpha^2d_e$ where $R_{rel} \sim 3$ is

the relativistic factor [35, 36]). This term corresponds to the atomic EDM due to the perturbation of the electron density by the operator \hat{H}_{2d} . Note that a similar equation with the perturbation \hat{H}_{1d} gives zero result due to exact cancellation between the first and second terms. Indeed, the zero and the first order corrections to the atomic EDM induced by \hat{H}_{1d} give EDM

$$\begin{aligned} \mathbf{D}_1 &= d_e \langle 0 | \sum \Sigma_i | 0 \rangle + \\ &e \sum_n \frac{\langle 0 | [\hat{Q}, \hat{H}_0] | n \rangle \langle n | \sum \mathbf{R}_i | 0 \rangle}{E_0 - E_n} + \\ &e \sum_n \frac{\langle 0 | \sum \mathbf{R}_i | n \rangle \langle n | [\hat{Q}, \hat{H}_0] | 0 \rangle}{E_0 - E_n} \end{aligned} \quad (33)$$

The above expression can be simplified in the following way. For the matrix elements of the commutators the following relations are valid

$$\langle n | [\hat{Q}, \hat{H}_0] | 0 \rangle = -(E_0 - E_n) \langle n | \hat{Q} | 0 \rangle \quad (34)$$

$$\langle 0 | [\hat{Q}, \hat{H}_0] | n \rangle = (E_0 - E_n) \langle 0 | \hat{Q} | n \rangle \quad (35)$$

Substituting these expressions into Eq. (32) and using the completeness condition $\sum |n\rangle \langle n| = \hat{1}$ we obtain

$$\begin{aligned} \mathbf{D}_1 &= e \sum_n \sum_i \left[\langle 0 | \hat{Q} | n \rangle \langle n | \mathbf{R}_i | 0 \rangle - \langle 0 | \mathbf{R}_i | n \rangle \langle n | \hat{Q} | 0 \rangle \right] + \\ &d_e \langle 0 | \sum \Sigma_i | 0 \rangle = d_e \langle 0 | \sum \Sigma_i | 0 \rangle + \sum_i e \langle 0 | [\hat{Q}, \mathbf{R}_i] | 0 \rangle \end{aligned} \quad (36)$$

Using definition of the operator \hat{Q} it is easy to show that $[\hat{Q}, \mathbf{R}_i] = -d_e/e \Sigma_i$. Hence, the second term in the above equation cancels the first term, so the dipole moment \mathbf{D}_1 induced by H_{1d} equals to zero. In this derivation we assume that the electron states are stationary. This is valid if we neglect the ion acceleration. Therefore, the result is consistent with Eq. (31).

We see that EDM of an ion induced by the electron EDM is given by the same equation (32) as for neutral atoms (up to corrections $\sim m_e/M_N$). A similar conclusion is also valid for molecular ions.

III. NUCLEAR EDM AND SCHIFF MOMENT IN MOLECULAR IONS

Let us consider a molecular ion with N_e electrons and two nuclei with charges Z_1e and Z_2e . We assume that the second nucleus has EDM \mathbf{d} and Schiff moment \mathbf{S} . The molecular Hamiltonian is equal to the sum of the

following terms:

$$\begin{aligned}
\hat{T} &= \sum_i^{N_e} \frac{-\hbar^2}{2m_e} \frac{\partial^2}{\partial \mathbf{R}_i^2} - \frac{\hbar^2}{2M_1} \frac{\partial^2}{\partial \mathbf{q}_1^2} - \frac{\hbar^2}{2M_2} \frac{\partial^2}{\partial \mathbf{q}_2^2}, \\
\hat{V}_0 &= \sum_{i>j}^{N_e} \frac{e^2}{|\mathbf{R}_i - \mathbf{R}_j|} - Z_2 e^2 \sum_i^{N_e} \int d^3r \frac{\rho(r)}{|\mathbf{R}_i - \mathbf{q}_2 - \mathbf{r}|} \\
&\quad - \sum_i^{N_e} \frac{Z_1 e^2}{|\mathbf{R}_i - \mathbf{q}_1|} + Z_1 Z_2 e^2 \int d^3r \frac{\rho(r)}{|\mathbf{q}_1 - \mathbf{q}_2 - \mathbf{r}|}, \\
\hat{V} &= \sum_i^{N_e} e \mathbf{R}_i \mathbf{E}_0 - Z_1 e \mathbf{q}_1 \mathbf{E}_0 - Z_2 e \mathbf{q}_2 \mathbf{E}_0, \\
\hat{U} &= -Z e^2 \sum_i^{N_e} \int d^3r \frac{\delta \rho(\mathbf{r})}{|\mathbf{R}_i - \mathbf{q}_2 - \mathbf{r}|}, \\
&\quad + Z_1 Z_2 e^2 \int d^3r \frac{\delta \rho(\mathbf{r})}{|\mathbf{q}_1 - \mathbf{q}_2 - \mathbf{r}|}, \\
\hat{W} &= -\mathbf{d} \mathbf{E}_0,
\end{aligned}$$

where \mathbf{q}_1 and \mathbf{q}_2 are the coordinates of first and second nuclei respectively. Using the operator

$$\hat{Q} = \frac{\mathbf{d}}{Z_2 e} \frac{\partial}{\partial \mathbf{q}_2} \quad (37)$$

we can present the molecular Hamiltonian in the form similar to Eq. (12):

$$\begin{aligned}
\hat{H} &= \hat{H}_0 + [\hat{Q}, \hat{H}_0] \\
&\quad - 4\pi e \mathbf{S} \left\{ \sum_i^{N_e} \nabla_i \delta(\mathbf{R}_i - \mathbf{q}_2) - Z_1 \frac{\partial}{\partial \mathbf{q}_1} \delta(\mathbf{q}_1 - \mathbf{q}_2) \right\}.
\end{aligned} \quad (38)$$

To calculate the average value of the commutator \hat{Q} and \hat{H}_0 we can use the same algorithm as for a single atom.

$$[\hat{Q}, \hat{H}_0] = -\frac{\mathbf{d}}{Z_2 e} \frac{i}{\hbar} [\hat{H}_0, \mathbf{P}_2] = -\frac{\mathbf{d}}{Z_2 e} M_2 \hat{\mathbf{a}}_2 \quad (39)$$

Since the molecule moves as a single body the average accelerations of all its particles is equal to the molecular acceleration, i.e.

$$\langle \hat{\mathbf{a}}_2 \rangle = \frac{\langle \mathbf{F} \rangle}{M_1 + M_2 + N_e m_e} \approx \frac{(Z_1 + Z_2 - N_e) e \mathbf{E}_0}{M_1 + M_2}, \quad (40)$$

$$\langle [\hat{Q}, \hat{H}_0] \rangle = -\frac{M_2}{M_1 + M_2} \frac{Z_1 + Z_2 - N_e}{Z_2} \mathbf{d} \mathbf{E}_0. \quad (41)$$

Finally, the effective Hamiltonian of the molecular ion is

$$\begin{aligned}
\hat{H} &= \hat{H}_0 - \frac{M_2}{M_1 + M_2} \frac{Z_1 + Z_2 - N_e}{Z_2} \mathbf{d} \mathbf{E}_0 \\
&\quad - 4\pi e \mathbf{S} \left\{ \sum_i^{N_e} \nabla_i \delta(\mathbf{R}_i - \mathbf{q}_2) - Z_1 \frac{\partial}{\partial \mathbf{q}_1} \delta(\mathbf{q}_1 - \mathbf{q}_2) \right\},
\end{aligned} \quad (42)$$

Thus, in a molecular ion the EDM term experiences the extra suppression. As for the Schiff moment term, it is still described by the same operator as for a single atom, except for the extra term proportional to $\partial(\delta(\mathbf{q}_1 - \mathbf{q}_2))/\partial \mathbf{q}_1$ describing the interaction of the charge of the first nucleus and the Schiff moment of the second nucleus. The matrix elements of such interaction are extremely small due to the Coulomb barrier.

IV. ENHANCEMENT OF THE SCHIFF MOMENT CONTRIBUTION TO P, T -ODD EFFECTS IN POLAR MOLECULES

Now we can compare the contributions of the nuclear EDM and Schiff moment to P, T -odd effects in polar molecular ions. Important difference between molecules and single atoms is that the nuclear motion significantly affects induced P, T -odd effects. The Schiff moment contribution in polar molecules is enhanced because of the strong internal electric field [25]. Another interpretation of the enhancement is due to the small distance between the opposite parity rotational levels [24, 29].

The nuclear P, T -odd effects are studied in the molecules with zero electron angular momentum. After averaging Hamiltonian Eq. (42) over electron wave function we obtain the effective Hamiltonian for the nuclear motion:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \Delta_q + U_e + \frac{\mu \omega^2}{2} (q - q_e)^2 + B J(J+1) + \hat{H}_w \quad (43)$$

where $\mathbf{q} = \mathbf{q}_1 - \mathbf{q}_2$, q_e is the equilibrium distance between the nuclei in averaged potential, J is the rotational angular momentum of the molecule, U_e describes the interaction of the partially screened nuclear EDM, the Schiff moment term \hat{H}_w can be presented as [24, 26]

$$\hat{H}_w = 6XS \frac{\mathbf{I} \cdot \mathbf{n}}{I}, \quad (44)$$

where $\mathbf{S} = S\mathbf{I}/I$, \mathbf{n} is the unit vector along the molecular axis, X is the constant that appears after averaging the perturbation over the electron wave function. In the first order of the perturbation theory the Schiff term leads to the rotation state mixing

$$\psi^{(1)} = 6XS \frac{I_z}{I} \sum_{J' \neq J} \frac{\langle Jm | n_z | J'm \rangle}{E_J - E_{J'}} |J'm\rangle \quad (45)$$

where $\psi^{(0)} = |Jm\rangle$ is the unperturbed rotational wave function. Since the energy difference $E_J - E_{J'} = B\{J(J+1) - J'(J'+1)\}$ can be very small for rotation levels, the state mixing can be significant. This mixing induces EDM in the rotational state

$$D_z^S = 2\langle \psi^{(0)} | D_M n_z | \psi^{(1)} \rangle \quad (46)$$

$$\begin{aligned}
&= \frac{6XS D_M I_z}{IB} \frac{J(J+1) - 3m^2}{J(J+1)(2J-1)(2J+3)} \\
&\equiv K_m S I_z / I.
\end{aligned} \quad (47)$$

Here $\mathbf{D}_M = D_M \mathbf{n}$ is the internal EDM of the polar molecule. This formula is valid for $J \neq 0$. For $J = 0$ the induced EDM is

$$D_z^S = -\frac{2XS D_M I_z}{IB} \equiv K_m S I_z / I \quad (48)$$

There is also the screened nuclear EDM contribution D_z^d to P, T -odd molecular EDM (see Eq. (42)). Combining this contribution with the Schiff moment contribution D_z^S we obtained the P, T -odd part of the interaction of a molecular ion with the external electric field E_0 :

$$V = -\left(\frac{M_2}{M_1 + M_2} \frac{Z_1 + Z_2 - N_e}{Z_2} d - K_m S\right) \frac{\mathbf{IE}_0}{I} \quad (49)$$

This equation tells us that there is actually no enhancement of the electric field in the polar molecule since the electric field at the nucleus is suppressed $1/Z_2$ times rather than enhanced. However, there is huge enhancement of the Schiff moment contribution since the expression for the coefficient K_m contains in the denominator the rotational constant B which may be five orders of magnitude smaller than the interval between atomic levels of opposite parity.

Note that we can derive Eq. (49) treating E_0 as a perturbation. Therefore, the energy shift produced by the Schiff moment in Eq. (49) is actually proportional to the average polarization of the polar molecule in the electric field E_0 . In the small electric field it is linear in E_0 , however, in the high field it tends to the constant. This determines the saturation effect in the energy shift produced by the Schiff moment if we go beyond the weak electric field E_0 approximation (see Eq. (44) where the average polarization $n_z < 1$).

Using Eq. (49) we can compare molecular EDM induced by the screened nuclear EDM and the Schiff moment. Consider, for example, molecule PbF^+ since it has the same number of electrons as a well studied molecule TIF where the effect of the nuclear Schiff moment has been measured. The screened EDM term for PbF^+ is $D_N \sim 10^{-23} \eta e \cdot \text{cm}$ (EDM of F and EDM of odd isotope of Pb give comparable contributions since values of M/Z are approximately the same). To obtain the Schiff moment induced EDM in the ground state we need to estimate the constant K_m , given by Eq. (48). Since the molecular parameters are unknown for the ion we assume them to be of the order of their values for the neutral molecule TIF: $X \approx 8000$ a.u. [32, 37]. The values of the rotational constant $B = 1.025 \cdot 10^{-6}$ a.u. and dipole moment $D_M = 1.65$ a.u. for TIF are taken from [38]. Finally, substituting all the parameters into Eq. (48) we obtain $K_m = 5 \cdot 10^{10}$ a.u. Assuming the Schiff moment value for an odd isotope of Pb equal to $S = 10^{-8} \eta e \cdot fm^3$ [24] we obtain the value for the Schiff moment contribution $D_S \sim 10^{-20} \eta e \cdot \text{cm}$ which is three orders of magnitude larger than the nuclear EDM contribution $D_N \sim 10^{-23} \eta e \cdot \text{cm}$. As it was mentioned above, in the nuclei with the octupole deformation like Ra^{225} the Schiff moment is enhanced. Therefore, in molecular

ions like RaF^+ the Schiff moment induced EDM will be 5 orders of magnitude larger than the partially screened nuclear EDM.

V. CONCLUSIONS

Accurate treatment of the electron EDM effects shows that the T, P -odd EDM of atomic and molecular ions at high Z are dominated by the Z^3 enhanced relativistic correction effect, similar to neutral systems. The direct contribution of electron EDM is suppressed by the screening factor (m_e/M) where M is the ion mass.

The situation is different for the nuclear EDM. In atoms the nuclear EDM is screened by the factor Z_i/Z where Z_i is the ion charge. However, the nuclear EDM still dominates over the Schiff moment induced atomic EDM (with exception of heavy ions which contain nuclei with the octupole deformation like ^{225}Ra and ^{223}Rn where the Schiff moment is strongly enhanced).

In molecular ions the nuclear EDM screening is slightly stronger than in atomic ions, the screening factor is $(M_N/M)(Z_i/Z)$. At the same the Schiff moment contribution is enhanced $\sim M_N/m_e \sim 10^5$ times due to the mixing of the close rotational states of opposite parity. There is the additional Schiff moment enhancement in such molecular ions like RaF^+ . As a result, the Schiff moment contribution is $10^3 - 10^5$ times larger than the screened nuclear EDM contribution.

This combination of the large enhancement factors makes molecular ion experiments an attractive alternative to the atomic EDM experiments.

VI. APPENDIX

According to Eq. (16) in the limit of the point-like nucleus the Schiff moment potential and its matrix element are given by

$$\varphi_S(\mathbf{R}) = 4\pi \mathbf{S} \cdot \nabla \delta(\mathbf{R}) \quad (50)$$

$$\langle s | -e\varphi_S | p \rangle = 4\pi e \mathbf{S} \cdot (\nabla \psi_s^\dagger \psi_p)_{R=0} \quad (51)$$

For the solutions of the Dirac equation $(\nabla \psi_s^\dagger \psi_p)_{R \rightarrow 0}$ is infinite for a point-like nucleus. Therefore, for relativistic electrons it is necessary to account for the finite size of the nucleus and introduce a finite-size Schiff moment potential. An appropriate potential has been shown [27] to increase linearly inside the nucleus and vanish at the nuclear surface:

$$\varphi_S(\mathbf{R}) = -\frac{3\mathbf{S}' \cdot \mathbf{R}}{B} n(R), \quad (52)$$

where $B = \int n(R) R^4 dR \approx R_N^5/5$, R_N is the nuclear radius and $n(R)$ is a smooth function which is 1 for $R < R_N - \delta$ and 0 for $R > R_N + \delta$; $n(R)$ can be taken as proportional to the nuclear density ρ_0 (note that we can

choose any normalization of $n(r)$ since the normalization constant cancels out in the ratio n/B , see Eq. (52)).

Below we will accurately derive expression for the corrected Schiff moment S' that corresponds to the potential (52).

The P, T -odd part of the nuclear electrostatic potential with electron screening taken into account can be written in the following form (see e.g. [34] for the derivation):

$$\varphi(\mathbf{R}) = Z \int \frac{e\rho(\mathbf{r})}{|\mathbf{R}-\mathbf{r}|} d^3r + \mathbf{d} \cdot \nabla \int \frac{e\rho(\mathbf{r})}{|\mathbf{R}-\mathbf{r}|} d^3r \quad (53)$$

As it was shown in [27] the expansion of the Coulomb potential in (53) in terms of the Legendre polynomials gives the following dipole term in the potential:

$$\varphi^{(1)}(\mathbf{R}) = Ze\mathbf{R} \int_R^\infty \left(\frac{\langle \mathbf{r} \rangle}{R^3} - \frac{\mathbf{r}}{R^3} + \frac{\mathbf{r}}{r^3} + \frac{\langle r_i \rangle q_{ij}}{r^5} \right) \rho(\mathbf{r}) d^3r \quad (54)$$

We see that $\varphi^{(1)}(\mathbf{R}) = 0$ if $R > R_N$ (nuclear radius) since $\rho(\mathbf{R}) = 0$ in that region. Therefore, corresponding matrix elements will depend on the electron wave functions behavior inside the nucleus. All the electron orbitals for $l > 1$ are extremely small inside the nucleus. Therefore, we can limit our consideration to the matrix elements between s and p Dirac orbitals. We will use the following notations for the electron wavefunctions:

$$\psi(\mathbf{R}) = \begin{pmatrix} f(R)\Omega_{jlm} \\ -i(\boldsymbol{\sigma} \cdot \mathbf{n})g(R)\Omega_{jlm} \end{pmatrix} \quad (55)$$

where Ω_{jlm} is a spherical spinor, $\mathbf{n} = \mathbf{R}/R$, $f(R)$ and $g(R)$ are the radial functions. Using $(\boldsymbol{\sigma} \cdot \mathbf{n})^2 = 1$ we can write the electron transition density as

$$\rho_{sp}(\mathbf{R}) = \psi_s^\dagger \psi_p = \Omega_s^\dagger \Omega_p U_{sp}(R) \quad (56)$$

$$U_{sp}(R) = f_s(R)f_p(R) + g_s(R)g_p(R) = \sum_{k=1}^\infty b_k R^k \quad (57)$$

The expansion coefficients b_k can be calculated analytically [27]; the summation is carried over odd powers of k . Using Eqs. (54,56) we can find the matrix elements of the electron-nucleus interaction,

$$\begin{aligned} \langle s | -e\varphi^{(1)}(\mathbf{R}) | p \rangle &= -Ze^2 \langle s | \mathbf{n} | p \rangle \cdot \left\{ \int_0^\infty [(\langle \mathbf{r} \rangle - \mathbf{r}) \cdot \right. \\ &\quad \left. \int_0^r U_{sp} dR + \left(\frac{\mathbf{r}}{r^3} + \frac{\langle r_i \rangle q_{ij}}{r^5} \right) \int_0^r U_{sp} R^3 dR \right] \rho d^3r \Big\} = \\ &= -Ze^2 \langle s | \mathbf{n} | p \rangle \cdot \left\{ \sum_{k=1}^\infty \frac{b_k}{k+1} \left[\langle \mathbf{r} \rangle \langle r^{k+1} \rangle - \frac{3}{k+4} \langle \mathbf{r} r^{k+1} \rangle \right. \right. \\ &\quad \left. \left. + \frac{k+1}{k+4} \langle r_i \rangle \langle q_{ij} r^{k-1} \rangle \right] \right\}, \quad (58) \end{aligned}$$

where $\langle s | \mathbf{n} | p \rangle = \int \Omega_s^\dagger \mathbf{n} \Omega_p d\phi \sin \theta d\theta$, $\langle r^n \rangle = \int \rho(\mathbf{r}) r^n d^3r$. Note, that all vector values $\langle \mathbf{r} r^n \rangle$ are due to P, T -odd correction $\delta\rho$ to the nuclear charge density ρ_0 , while $\langle r^n \rangle$ are the usual P, T -even moments of the charge density starting from the mean-square radius $\langle r^2 \rangle = r_q^2$ for $k = 1$.

We now set the matrix elements (58) of the true nuclear T, P -odd potential to be equal to the matrix elements of the equivalent potential (52) which are given by

$$\begin{aligned} \langle s | -e\phi(\mathbf{R}) | p \rangle &= 15e \langle s | \mathbf{n} | p \rangle \cdot \frac{\mathbf{S}'}{R_N^5} \int_0^\infty U_{sp} R^3 n(R) dR \\ &= 15e \langle s | \mathbf{n} | p \rangle \cdot \mathbf{S}' \sum_{k=1}^\infty b_k \frac{R_N^{k-1}}{k+4}, \end{aligned} \quad (59)$$

where we have made approximation $\int n(R) R^k dR \approx R_N^{k+1}/(k+4)$. Equating (58) and (59) we obtain

$$\begin{aligned} \mathbf{S}' &= \frac{Ze}{15} \frac{1}{\sum_{k=1}^\infty \frac{b_k}{b_1} \frac{1}{k+4} R_N^{k-1}} \sum_{k=1}^\infty \frac{b_k}{b_1} \frac{1}{k+1} \\ &\quad \left[\frac{3}{k+4} \langle \mathbf{r} r^{k+1} \rangle - \langle \mathbf{r} \rangle \langle r^{k+1} \rangle - \frac{k+1}{k+4} \langle r_i \rangle \langle q_{ij} r^{k-1} \rangle \right] \end{aligned} \quad (60)$$

Thus we have a possibility of separating the nuclear and electronic parts of the calculation of atomic EDMs. The nuclear calculation involves only the determination of \mathbf{S}' and the atomic calculation involves only the effects produced by the equivalent potential (52).

Note that \mathbf{S}' in eq. (60) is different from the Local dipole moment L defined in Ref. [27]: L does not contain the sum in the denominator. The reason for the difference is that here we reduce the problem to the nuclear size effective potential (52) while in Ref. [27] the problem was reduced to the contact effective potential (50) located in the center of the nucleus.

In the non-relativistic case ($Z\alpha \rightarrow 0$) we have just $b_1 \neq 0$, and

$$\lim_{Z\alpha \rightarrow 0} \mathbf{S}' = \frac{Ze}{10} \left[\langle \mathbf{r} r^2 \rangle - \frac{5}{3} \langle \mathbf{r} \rangle \langle r^2 \rangle - \frac{2}{3} \langle r_i \rangle \langle q_{ij} \rangle \right]. \quad (61)$$

This is the usual expression for the Schiff moment \mathbf{S} . In practice it may be sufficient to use only the first and third terms in the expansion of U_{sp} . In this case we need only the ratio b_3/b_1 . This ratio is different for the matrix elements $s - p_{1/2}$ ($b_3/b_1 = -(3/5)Z^2\alpha^2/R_N^2$) and $s - p_{3/2}$ ($b_3/b_1 = -(9/20)Z^2\alpha^2/R_N^2$). However, with the 10% accuracy we can use the average of these two values $b_3/b_1 \approx -0.5Z^2\alpha^2/R_N^2$.

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